

**IONICALLY COMPLEXED COLORANTS AND METHODS OF MAKING AND
USING SAME**

5

FIELD OF THE INVENTION

The invention relates to colorants. More specifically, the invention relates to colorants comprising ionic dye components, and methods of making and using same.

10

BACKGROUND

Colorants have been used since the dawn of time by humankind as a way to express ideas and to modify and decorate the surrounding world. For example, colorant compositions were used to draw images on various surfaces, from cave walls to papyrus sheets to modern paper and canvas. Additionally, colorant compositions have been used to impart color to articles and surfaces, such articles as tools, toys, fabrics and plastic sheets, and on structural surfaces such as walls, floors and ceilings. To this end, colorants have been incorporated into ink and paint compositions, and in preconcentrate compositions for incorporation into articles made from plastics and the like.

20

Various colorants have been developed over the years, and are generally characterized in the classes of dyes, pigments and lakes. A dye is defined in Webster's dictionary as "a usually soluble substance for staining or coloring e.g. fabrics or hair." Likewise, Webster's defines pigment as "dry coloring matter (especially an insoluble powder to be mixed with a liquid to produce paint etc)." A lake is defined as "A pigment formed by combining some coloring matter, usually by precipitation, with a metallic oxide or earth, esp. with aluminium hydrate; as, madder lake; Florentine lake; yellow lake, etc." Lake pigments are conventionally prepared by the precipitation of a soluble organic dye on to an insoluble, inorganic, adsorptive substrate. The pigment is formed by the chemical reaction that occurs when a suitable reagent, such as alum, is added to an aqueous solution containing the dyestuff and, usually, one or more other chemicals, such as sodium or potassium carbonate.

30

Permanent pigments are sought in the art to provide lasting color in various applications. For example, U.S. Patent No. 4,576,649 to Oliver, et. al. discloses preparation of permanent pigments from selected cationic dyes by precipitation from aqueous solution with complex heteropoly acids in the presence of selected amine color enhancing agents. These pigments are stated to be of interest in formulating high quality lithographic inks.

In a particular use, colorants are desired for incorporation into toners for electrostatographic printing and copying processes. For example, U.S. Patent No. 5,434,030 to Smith, et al. discloses a toner composition including a resin, a charge enhancing additive, an ion binding polymer, and at least one ionic dye complexed to the ion binding polymer. The ionic dye is a component that is different from the charge enhancing additive, and is stabilized and dispersed in the toner composition.

U.S. Patent No. 5,766,269 to Berenguer, et. al. describes cationic dyes comprising at least one quaternary ammonium group or protonated or protonizable tertiary amino group and at least one chromophoric radical, wherein the chromophoric radical is the radical of an optionally (pre)reduced sulphur dye, its precursor containing a cationic group which is a secondary amino group of basic character. These dyes are stated to be combinable with an anionic desolubilizer to form a water insoluble dye. Examples of desolubilizers include, among other examples, anionic dyes. See column 15, lines 37-50.

U.S. Patent No. 6,001,524 to Yoon discloses toner particles for color electrophotographic imaging applications. The particles are based on substantially amorphous polyesters that contain functionalities that are capable of being reacted with coloring reagents to form dyed polyester particles, which after further treatment are incorporated into toner compositions.

25

SUMMARY OF THE INVENTION

It has been found that ionically complexed colorant compounds may be provided wherein an ionic dye component having an apparent color characteristic is ionically complexed with a first dye counterion component having a known color characteristic that exhibits a color difference from the ionic dye component of at least about 10 ΔE^* units and a colorless counterion component. For purposes of the present invention, a

30

colorless counterion component is a component that under conditions of use does not exhibit a color in the visible light range. The ionic dye component is ionically complexed with the first dye counterion and colorless counterion in a predetermined ratio to form an ionically complexed colorant compound exhibiting a predetermined color.

5 For purposes of the present invention, a composition is stated to have an apparent color when evaluated in a manner to indicate the color that an observer under ordinary viewing conditions for the composition would ascribe to that composition, notwithstanding individual color inhomogeneities that might otherwise be observed when examining at higher magnifications. A dye component is an ion (or counterion) that
10 exhibits an apparent color in the visible light range to the ordinary observer.

Compositions comprising these compounds are also provided. Methods of preparing these compositions, and methods of use of these compositions are also provided. Additionally, compositions are provided comprising an ionic dye, a first dye counterion component having a known color characteristic that exhibits a color difference from the
15 ionic dye component of at least about 10 ΔE^* units and a colorless counterion component, wherein the ionic dye component is ionically complexed with the first dye counterion component and colorless counterion component in a predetermined ratio to form ionically complexed compounds that together in a colorant composition exhibit a predetermined color.

20 The compounds and compositions of the present invention provide unique colorant chemistries not previously known. These chemistries present advantages in formulation opportunities through the ability to use materials having unique solubility properties both prior to and after complexation. The resulting colorant preferably exhibits less migration from the composition to undesired environments, such as staining
25 various surfaces in which the composition may come in contact. Additionally, the colorants of the present invention surprisingly can be formulated to have low solubility or be substantially insoluble in water and/or another selected colorant carrier solvent. In one aspect, compounds of the present invention optionally may additionally be complexed with a metal ion. However, in a more preferred aspect of the present invention, low
30 solubility in water and/or another colorant carrier solvent may optionally be achieved by compounds that do not contain heavy metals. Thus, the present invention in a preferred

aspect provides an "organic lake," meaning that the colorant compound is substantially free of inorganic metal counterions.

The present invention additionally provides substantial benefit in easily expanding the choice of colors for use in various applications. Colorants are always subject to testing to determine the effect of the chemistries employed on our environment, and also specifically on human health through direct contact or ingestion of the colorant. The identification and approval of new colors may be an expensive and drawn out clearing process due to the above concerns. The present invention allows the preparation of new colors without the need to create totally new molecules that require a full *de novo* clearance process. Instead, new colors may now be formed by complexing previously known (and preferably already cleared) dye molecules to form an apparently new color that incorporates partially old chemistry. Additionally, the apparent color of the composition may be fine-tuned to the exact desired hue by adjusting relative dye content as taught herein. Because the dye components are complexed to each other, the resulting color is stable in most environmental conditions without concern of differential chemical properties leading to a change in ratio of the different dyes as may occur in dye blends that are merely physically blended.

Additionally, because a great portion of the colorant compound comprises material that contributes to the apparent color, colorants of the present invention may exhibit surprisingly high color saturation and/or brilliance as compared to conventional lakes or other colorants.

DETAILED DESCRIPTION

Colorants of the present invention exhibit a color that is visible and apparent to the human eye. The actual color exhibited may be measured and/or evaluated using any appropriate technique suitable for the particular application. One such color measuring technique is the CIE $L^*A^*B^*$ color system, as described in "Principles of Color Technology", Billmeyer & Saltzman, Second Edition, 1981. This system is based on a 3-dimensional color space with the positive X-axis representing red, the negative X-axis representing green, the positive Y-axis representing yellow, the negative Y-axis representing blue, and the Z-axis going from zero (black) to 100 (white) with the origin at

50. The CIE ΔE^* (hereafter " ΔE^* "), is defined as a measure of color difference, namely the Euclidean distance or the straight line distance between two colors that are expressed by the Lab coordinates.

Because the CIE Lab color-space would be a perceptually uniform color-space,
5 then the Euclidean distance between two colors in this space would be a perceptually uniform measure for color-difference. The ΔE^* is calculated as:

$$\Delta E^* = [(L1-L2)^2 + (a1-a2)^2 + (b1-b2)^2]^{(1/2)} \text{ where:}$$

L1, a1 and b1 are the Lab values of color 1 and

L2, a2 and b2 are the Lab values of color 2.

10 In this measurement system, it can be generally stated that if two samples have a measured color difference of at least about 10 ΔE^* units, this color difference is of a degree that can be observed by the human eye.

In the present invention at least two of the dye components when measured separately exhibit a color difference of at least about 10 ΔE^* units. The resulting color of
15 the colorant complex is therefore a mixture of the apparent colors of each of the dye components. In a particularly preferred embodiment of the present invention, at least two of the dye components exhibit a color difference of at least 20 ΔE^* units. Thus, in this embodiment, the degree of difference in color of each component from the other (when evaluated in a side-by-side manner, rather than in a blended fashion) would be quite
20 apparent to visible perception. However, due to the close proximity of the dye components to each other in the complexed compound, the apparent resulting color of the colorant is a blend of the two colors. This embodiment of the present invention provides a high precision of color matching and stability, with little or no issues of color separation that might be observed by merely blending two or more individual colorants that may
25 have different solubility or dispersibility characteristics from each other.

In a preferred embodiment of the present invention, the colorless counterion component of the ionically complexed colorant compound is a relatively small portion of the overall colorant. This embodiment is of benefit, because a larger portion of the colorant actually contributes to the effective color that is observed, providing a more
30 effective colorant that can be present as a smaller amount in the overall ultimate composition, while still having the desired colorant effect. In one preferred embodiment,

the colorless counterion component comprises less than about 40% of the total colorant compound by weight. In another preferred embodiment, the colorless counterion component comprises less than about 20% of the total colorant compound by weight. In another preferred embodiment, the colorless counterion component comprises less than about 10% of the total colorant compound by weight.

In a preferred embodiment of the present invention, the ionically complexed colorant compound is substantially free of metal that is not covalently bound to the colorant compound. This is of particular benefit because such colorant compositions avoid the use of metals, and particularly heavy metals that may dissociate from the colorant compound and cause compositional disturbances or instability, such as charge imbalances, or raise health concerns.

Preferably, the ionically complexed colorant compound or composition has a water solubility of less than 100 parts per million. In addition, preferably the ionically complexed colorant compound or composition has a solubility in various carrier solvents such as ketones, alcohols, esters, glycol ethers and esters, aliphatic and aromatic hydrocarbons and the like of less than 100 parts per million.

In one embodiment of the present invention, the colorant comprises a combination of three or more dyes, in addition to the colorless component. In such a system, an ionic dye is complexed with a first and second counterion dye. For example, a cationic dye may be complexed with a first anionic dye, a second anionic dye and an anionic colorless component. In a preferred embodiment, the first ionic dye comprises a plurality of ionic functionalities on the ionic dye component, so that a single ionic dye component is capable of coordinating with a plurality of counterions. In a preferred embodiment, all of the dyes in the colorant exhibit a color difference of at least about 20 ΔE^* units from each other. The apparent color of the colorant may be adjusted by varying the relative amounts of first counterion dye and second counterion dye in the total colorant composition. The apparent color of the colorant composition is modulated by incorporation of more or less of the colorless counterion as desired. Preferably, the colorless counterion is an organic counterion. The use of a plurality of dye counterions in particular provides a high precision of color matching, with little or no issues of color

separation that might be observed by merely blending two or more individual colorants that may have solubility or dispersibility characteristics that are different from each other.

In a particularly preferred embodiment, the ionically complexed colorant compound contains no polymeric components. Such a compound is of particular benefit because it is easier to assure full coordination of all ionic sites when reacting only monomeric materials. Thus, larger compounds may have a tendency to prematurely insolubilize during the dye binding process prior to coordination of all ionic sites. Ionomers in particular may prematurely agglomerate before the desired colorant compound is formed. The presence of uncomplexed sites on a polymeric component may additionally provide regions of instability with respect to moisture, which may be problematic particularly if the final application of the colorant is in an environment where the colorant is exposed to moisture through, for example, skin contact or ambient humidity. The resulting image may be tacky or sensitive to water. Additionally, non-polymeric colorant compounds may be easier to process, handle, mill to the desired size and consistency and disperse into various resins or compositions. Further, colorant compositions that do not contain polymeric components do not provide an additive Tg that may adversely affect the predetermined balance of the binder. In a preferred embodiment, the colorant compound has a molecular weight of less than about 5000 Daltons. In another preferred embodiment, the colorant compound has a molecular weight of less than about 3000 Daltons.

Preferably, the colorant is a single compound having the ionic dye, the dye counterion and the colorless counterions components complexed at the preselected ratio, so that each compound *per se* will have the desired ratio of components to achieve the desired apparent color. It will be understood that some ion exchange may occur in situ, or that in some preparation processes some compound pairs or groups may be formed, so that one compound of the pair will comprise a plurality of dye counterions and the other compound of the pair will comprise a plurality of the colorless counterion, so that the pair taken together exhibits the desired apparent color. Likewise, a grouping of three or more compounds may be formed in a like manner, so that the group taken together exhibits the desired apparent color. For purposes of the present invention, a certain amount of this

pairing or grouping is contemplated on a molecular level, and the pair or group is considered to be within the scope of a colorant compound as described herein.

In another embodiment of the present invention, predetermined combinations of complexed dyes, dye counterions and colorless counterions may be prepared to ionically coordinate all components in the desired ratio in a single composition, without regard to whether these components are complexed with each other in a single compound. In this embodiment, preferably all ionic components are ionically complexed so that each compound in the composition is insoluble in water and in the carrier liquid of the ultimate coloring composition, so that no separation of the compounds from each other occurs under manufacture or use conditions. These colorant compositions may be formulated with additional ingredients and used in the manner of the compounds as described herein.

The anionic dyes to be used in the present invention may be any dye having a negative charge that is capable of complexing with a cationic counterion as taught herein. In one aspect of the present invention, the anionic dye comprises a plurality of negatively charged functionalities, sterically located so that the anionic dye is capable of complexing with a plurality of cationic counterions. Preferred anionic dyes are those that contain one or more sulfonate groups, carboxyl groups and/or hydroxyl salt groups. Examples of such anionic dyes include, but are not limited to, sulfonate salts of phthalocyanine, azo-, pyrazoline and anthraquinone dyes, and mixtures thereof. Additional examples of such anionic dyes include Acid Alizarin Violet, Acid Yellow 40, Acid Red 4, Acid Blue 25, Acid Violet 7, Phloxine B, copper phthalocyaninetetrasulfonic acid tetrasodium salt, Quinoline yellow, Acid yellow 17, Tartrazine, Alizarin Yellow GG, Reactive Black 5, Eosin Y, Erioglaucine, Acid Red 91, Acid Red 51, and Food Black 1.

The cationic dyes to be used in the present invention may be any dye having a positive charge that is capable of complexing with an anionic counterion as taught herein. In one aspect of the present invention, the cationic dye comprises a plurality of positively charged functionalities, sterically located so that the cationic dye is capable of complexing with a plurality of anionic counterions. Preferred cationic dyes to be used in the present invention contain one or more quaternary ammonium, sulfonium, phosphonium and oxonium groups. Examples of such cationic dyes include, but are not limited to, Tetrazolium Violet, Rhodamine B, Indoine Blue, Auramine 0, mixtures

thereof and the like. Additional examples of such cationic dyes are selected from the group consisting of Color Index Basic Red 12, Color Index Basic Red 14, Color Index Basic Red 28 and Color Index Basic Violet 10, Basic Yellow 1, Alcian Blue-tetrakis(methylpyridium) chloride, Basic Blue 41 and Basic Red 1.

5 The colorless counterion component may be any colorless counterion that is capable of complexing with the dye ion as taught therein. Preferably, the colorless counterion is an organic counterion. In a preferred embodiment, the colorless counterion comprises a plurality of functionalities available for coordination with the dye, so that a plurality of dye ions may be complexed with a single colorless counterion. The colorless
10 counterion, when the dye to be complexed with is an anion, preferably is a cationic compound selected from quaternary ammonium salts, sulfonium salts, phosphonium salts, oxonium salts, and any combination thereof of alkyl, aryl and alkyl/aryl compounds. The colorless counterion, when the dye to be complexed with is a cation, preferably is an anionic compound selected from sulfonates, carboxylates, hydroxyl salts
15 and any combination thereof of alkyl, aryl and alkyl/aryl compounds.

 In a particularly preferred embodiment of the present invention, the ionic dyes are selected so that the ultimate colorant compound exhibits the apparent color of either yellow, magenta, cyan, or black. These colors are the four colors used in traditional printing presses. By using well recognized combinations or blends of these four colors,
20 nearly all desired colors can be obtained. The present invention provides a system for provision of stable and reproducible colorants of each of these four colors, which is a significant benefit to the art.

 In a preferred embodiment of the present invention, the ionic dye and colorless colorant components are water soluble prior to being complexed with each other. When
25 these components are combined, preferably a water insoluble precipitate is formed. Optionally, a water miscible solvent may be added to increase solubility of one or more of the ionic components prior to complexation, particularly where the concentration of reactants in the reaction composition is high in order to reduce the volume of the reactant solution to a manageable level. After precipitation, the counterions that were associated
30 with the anionic and cationic reactants remain in solution. The precipitate is isolated by filtration and preferably washed with more water to remove any remaining soluble

counterions. This washing process optionally may be repeated several times. The precipitate is then dried and can then be used as a colorant. Preferably, the colorants of the present invention are not soluble in water. Water insolubility both eases handling of the colorant, and also provides a benefit in reducing the amount of staining of various surfaces and/or sensitivity to humidity during subsequent application or use of the colorant.

Colorants of the present invention may be used in any application where imparting a color is desired. Examples of such uses include as part of a material to transfer images and messages to various surfaces, and as a colorant to impart color to articles and surfaces, including articles such as tools, toys, fabrics and plastic sheets, and on structural surfaces such as walls, floors and ceilings.

In a preferred application, the colorant is provided in a vehicle in liquid or paste form as a coatable colorant composition for application to a surface to impart a color, for example as a coating, ink or paint composition. Such a colorant composition may be applied to any suitable surface, such as leather, fabric, paper, polymeric surface, metal surface and the like, as will be apparent to the artisan. The colorant preferably is provided together with a binder in a homogeneous composition or as a suspension. Preferably, the colorant is provided together in close association with a binder, for example in the form of a colorant/binder particle such as a toner particle. In a particularly preferred embodiment, the colorant of the present invention is provided in a latex paint composition. Latex paint conventionally comprises pigments, binders, liquid carriers including water, and additives (such as surfactants). Paint compositions in general are known in the art, and may be readily formulated by the routineer to incorporate colorants of the present invention by reference to the present disclosure. Preferably, the binder of the latex paint composition comprises styrene-butadiene polymers, vinyl acrylic polymers or acrylic polymers, or combinations thereof as are known in the art.

Colorants of the present invention are particularly suited for use in toners used in the copying and printing industry. Most particularly, the present colorants are useful for incorporation in either liquid or dry toners for electrographic printing processes (including electrophotographic and electrostatic processes). The colorants are readily

compatible with desired toner chemistries, and further may result in toners that exhibit superior charge transfer characteristics. Electrophotographic printing processes use electrostatic transfer to move images made of discrete toner particles from one surface to the next. The charging of these toner particles is very important in this transfer process.

- 5 Ionic dyes that are complexed with another ionic dye, rather than a heavy metal ion, exhibit different charge and transfer properties, thereby providing opportunity for improvement in toner transfer.

When used as part of a toner composition, various suitable toner resins may be selected for incorporation with the colorant of the present invention. Illustrative
10 examples of typical resins include polyamides, epoxies, polyurethanes, vinyl resins, polycarbonates, polyesters, and the like and mixtures thereof. Any suitable vinyl resin may be selected including homopolymers or copolymers of two or more vinyl monomers. Typical examples of such vinyl monomeric units include: styrene; vinyl naphthalene; ethylenically unsaturated mono-olefins such as ethylene, propylene, butylene, isobutylene
15 and the like; vinyl esters such as vinyl acetate, vinyl propionate, vinyl benzoate, vinyl butyrate and the like; ethylenically unsaturated diolefins, such as butadiene, isoprene and the like; esters of unsaturated monocarboxylic acids such as methyl acrylate, ethyl acrylate, n-butyl acrylate, isobutyl acrylate, dodecyl acrylate, n-octyl acrylate, phenyl acrylate, methyl methacrylate, ethyl methacrylate, butyl methacrylate and the like;
20 acrylonitrile; methacrylonitrile; vinyl ethers such as vinyl methyl ether, vinyl isobutyl ether, vinyl ethyl ether and the like; vinyl ketones such as vinyl methyl ketone, vinyl hexyl ketone, methyl isopropenyl ketone and the like; and mixtures thereof. Also, there may be selected as toner resins various vinyl resins blended with one or more other resins, preferably other vinyl resins, which insure good triboelectric properties and
25 uniform resistance against physical degradation. Furthermore, nonvinyl type thermoplastic resins may also be employed including resin modified phenolformaldehyde resins, oil modified epoxy resins, polyurethane resins, cellulosic resins, polyether resins, polyester resins, and mixtures thereof.

Preferably, the toner comprises an amphipathic graft copolymer that has been
30 dispersed in a liquid carrier to form an organosol, then mixed with other ingredients to form a liquid toner composition. Typically, organosols are synthesized by nonaqueous

dispersion polymerization of polymerizable compounds (e.g. monomers) to form copolymeric binder particles that are dispersed in a low dielectric hydrocarbon solvent (carrier liquid). These dispersed copolymer particles are sterically-stabilized with respect to aggregation by chemical bonding of a steric stabilizer (e.g. graft stabilizer), solvated by the carrier liquid, to the dispersed core particles as they are formed in the polymerization. Details of the mechanism of such steric stabilization are described in Napper, D.H., "Polymeric Stabilization of Colloidal Dispersions," Academic Press, New York, N.Y., 1983. Procedures for synthesizing self-stable organosols are described in "Dispersion Polymerization in Organic Media," K.E.J. Barrett, ed., John Wiley: New York, N.Y., 1975.

Liquid toner compositions have been manufactured using dispersion polymerization in low polarity, low dielectric constant carrier solvents for use in making relatively low glass transition temperature ($T_g < 30^\circ\text{C}$) film-forming liquid toners that undergo rapid self-fixing in the electrophotographic imaging process. See, e.g., U.S. Pat. No. 5,886,067 and 6,103,781. Organosols have also been prepared for use in making intermediate glass transition temperature (T_g between 30 - 55°C) liquid electrostatic toners for use in electrostatic stylus printers. See, e.g., U.S. Pat. No. 6,255,363 B1. A representative non-aqueous dispersion polymerization method for forming an organosol is a free radical polymerization carried out when one or more ethylenically-unsaturated monomers, soluble in a hydrocarbon medium, are polymerized in the presence of a preformed, polymerizable solution polymer (e.g. a graft stabilizer or "living" polymer). See U.S. Pat. No. 6,255,363.

Once the organosol has been formed, one or more additives can be incorporated, as desired. For example, one or more visual enhancement additives and/or charge control agents can be incorporated. The composition can then subjected to one or more mixing processes, such as homogenization, microfluidization, ball-milling, attritor milling, high energy bead (sand) milling, basket milling or other techniques known in the art to reduce particle size in a dispersion. The mixing process acts to break down aggregated visual enhancement additive particles, when present, into primary particles (having a diameter in the range of 0.05 to 5 microns) and may also partially shred the dispersed copolymeric

ociate with the surface of the visual

persed copolymer or fragments derived
ual enhancement additive, for example, by
usual enhancement additive, thereby
ly-stabilized, nonaqueous dispersion of
diameter (determined with laser
50.0 microns, more preferably in the range
y in the range of about 1.5 to about 5
harge control agents can be added before

ompositions are important to provide high
characteristics are especially important to

Further, rapid self-fixing of the toner
liquid electrophotographic printing
h as smearing or trailing-edge tailing) and
example, in organosol toner compositions
formed during the imaging process may be
utions. This may result in image splitting
r intermediate image receptor surfaces.

g a liquid toner composition relates to the
final receptor. Erasure resistance, e.g.
mage by abrasion, particularly by abrasion
only used to remove extraneous pencil or
uid toner particles.

ay alternatively be dispersed within a
n the matrix. For example, colorants may
s, which are then processed to form fibers,
chniques known in the art. For example,
aning, and melt spinning techniques.

d/or calendaring processes and the like,

and solid forms may be formed by injection molding, rotational molding, and the like. The resulting article thereby exhibits an apparent color due to the presence of the colorant of the present invention. Likewise, color may be provided to articles made by alternative matrix materials, such as wax for forming wax candles, and the like.

5 • In order to facilitate mixing into a final matrix composition, preferably colorants of the present invention are provided as a color pre-concentrate composition comprising the colorant in a small amount of material that is compatible with the matrix material that is ultimately to comprise the colorant. This color pre-concentrate composition preferably is provided in the form of a dry powder, a liquid, a pelletized concentrate or as mini-
10 beads. For example, if the ultimate matrix is to be formed of a polyester, the pre-concentrate preferably comprises polyester material. Likewise, if the matrix is to be formed from wax, the pre-concentrate preferably comprises a wax material. Preferably, the colorant is provided in a concentration of about 20% to about 60% by weight, when provided as a pre-concentrate.

15 Alternatively, the colorant may be dispersed within a combination matrix, such as fibers and the like, in order to provide colored materials. An example of such a matrix is paper, which comprises cellulose fibers and a binder system to hold the fibers together. Colorant of the present invention may optionally be dispersed in the matrix, thereby providing the article with an apparent color.

20 All patents, patent documents, and publications cited herein are incorporated by reference as if individually incorporated. Unless otherwise indicated, all parts and percentages are by weight and all molecular weights are weight average molecular weights. The foregoing detailed description has been given for clarity of understanding only. No unnecessary limitations are to be understood therefrom. The invention is not
25 limited to the exact details shown and described, for variations obvious to one skilled in the art will be included within the invention defined by the claims.